JC08 Rec'd PCT/PTO 0 2 MAR 2001

FORM PTO-1390 (REV. 11-2000) U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		ATTORNEY'S DOCKET NUMBER Mo-6259/PS-1046 U S APPLICATION NO. (If known, see 37 CFR 1 5 09/786408
INTERNATIONAL APPLICATION NO. PCT/CA99/00804	INTERNATIONAL FILING DATE September 3, 1999	PRIORITY DATE CLAIMED September 4, 1998

TITLE OF INVENTION Gel Reduction in High Cis-1,4-Polybutadiene Production Process

APPLICANT(S) FOR DO/EO/US OSMAN, Akhtar and BARSAN, Florin

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND or SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. ☒ is attached hereto (required only if not communicated by the International Bureau).
   b. ☐ has been communicated by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. ☐ is attached hereto.
   b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Aplication under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. ☐ are attached hereto (required only if not communicated by the International Bureau).
   b. ☐ have been communicated by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English lanugage translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
14. ☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:

Notarial Certificate of true Copy of Document (Assignment)

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APPLICATION NO (if known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER
09/786408 To Be Assigned	PCT/CA99/00804	Mo-6259/PS-1046

21. [X] The following fees are submitted:	CALCULATIONS	PTO USE ONLY
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):		
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a (2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **$1000.00**		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **$860.00**		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **$710.00**		
International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$690.00**		
International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) **$100.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 860.00	
Surcharge of **$130.00** for furnishing the oath or declaration later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$ 0.00	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	$	
Total claims	32 -20 =	12	**x $18.00**	$ 216.00	
Independent claims	1 -3 =	0	**x $80.00**	$ 0.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			**+ $270.00**	$ 0.00	
TOTAL OF ABOVE CALCULATIONS =				$ 1,076.00	
[ ] Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2. +				$ 0.00	
SUBTOTAL =				$ 1,076.00	
Processing fee of **$130.00** for furnishing the English translation later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				$ 0.00	
TOTAL NATIONAL FEE =				$ 1,076.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property +				$ 40.00	
TOTAL FEES ENCLOSED =				$ 1,116.00	
				Amount to be refunded:	$
				charged:	$

a. [ ] A check in the amount of $ ____________ to cover the above fees is enclosed.

b. [X] Please charge my Deposit Account No. 13-3848 in the amount of $ 1,116.00 to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 13-3848. A duplicate copy of this sheet is enclosed.

d. [ ] Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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00157
PATENT TRADEMARK OFFICE

SIGNATURE

N. Denise Brown
NAME

36,097
REGISTRATION NUMBER

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PATENT APPLICATION
Mo6259
PS-1046

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF)	PCT/CA99/00804
AKHTAR OSMAN ET AL)	
SERIAL NUMBER: TO BE ASSIGNED)	
FILED: HEREWITH)	
TITLE: GEL REDUCTION IN HIGH CIS-1,4 POLYBUTADIENE PRODUCTION PROCESS)	

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Applicants respectfully request that the present application be amended as follows after assignment of a serial number and a filing date, but before examination.

IN THE CLAIMS:

Please cancel Claims 1-32.

Please add the following new Claims.

--33. A process for the production of cis-1,4-polybutadiene having a low level of gel content, comprising polymerizing 1,3-butadiene in the presence of a catalyst and a polymerization diluent, wherein the polymerization diluent comprises an organic solvent and water particles having a median particle size less than or equal to about 10 μm.

"Express Mail" mailing label number EL062670473US
Date of Deposit March 2, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231

Donna J. Veatch
(Name of person mailing paper or fee)

(Signature of person mailing paper or fee)

34. The process of Claim 33, wherein the water present in said polymerization diluent is present as particles having a median particle size in the range of from about 0.5 μm to about 8 μm.

35. The process of Claim 33, wherein the water present in said polymerization diluent is present as particles having a median particle size in the range of from about 0.5 μm to about 6 μm.

36. The process of Claim 33, wherein the water present in said polymerization diluent is present as particles having a median particle size in the range of from about 1 μm to about 5 μm.

37. The process of Claim 33, wherein the organic solvent of said polymerization diluent is selected from the group consisting of an aliphatic compound, an aromatic compound and mixtures thereof.

38. The process of Claim 37, wherein said aliphatic compound is selected from the group consisting of a saturated hydrocarbon, an unsaturated hydrocarbon and mixtures thereof.

39. The process of Claim 38, wherein the saturated hydrocarbon is selected from the group consisting of a C_4-C_{10} aliphatic hydrocarbon, a C_5-C_{10} cyclic aliphatic hydrocarbon, a C_6-C_9 aromatic hydrocarbon, a C_2-C_{10} monoolefinic hydrocarbon and mixtures thereof.

40. The process of Claim 39, wherein the C_4-C_{10} aliphatic hydrocarbon is selected from the group consisting of butane, pentane, hexane, heptane, octane and mixtures thereof.

41. The process of Claim 39, wherein the C_2-C_{10} monoolefinic hydrocarbon is selected from the group consisting of butene-1, pentene-1, hexene-1 and mixtures thereof.

42. The process of Claim 39, wherein the C_5-C_{10} cyclic aliphatic hydrocarbon is selected from the group consisting of unsubstituted cycloalkanes, methyl substituted cycloalkanes, ethyl substituted cycloalkanes and mixtures thereof.

43. The process of Claim 39, wherein the C_5-C_{10} cyclic aliphatic hydrocarbon is selected from the group consisting of cyclopentane, cyclohexane, cyclooctane and mixtures thereof.

44. The process of Claim 39, wherein the C_6-C_9 aromatic hydrocarbon is selected from the group consisting of benzene, toluene, xylene and mixtures thereof.

45. The process of Claim 33, wherein the organic solvent of said polymerization diluent comprises a mixture of cyclohexane and butene-1.

46. The process of Claim 33, wherein said polymerization diluent additionally comprises a polymerization modifier selected from the group consisting of C_2-C_{18} non-conjugated dienes, C_6-C_{12} cyclic dienes and mixtures thereof.

47. The process of Claim 46, wherein the polymerization modifier is selected from the group consisting of 1,2-butadiene, 1,3-cyclooctadiene, 1,5-cyclooctadiene and mixtures thereof.

48. The process of Claim 33, wherein said catalyst comprises a substantially anhydrous cobalt salt and an organo-aluminium halide compound.

49. The process of Claim 48, wherein the substantially anhydrous cobalt salt comprises a compound corresponding to the formula:

$$CoA_m$$

wherein:

A: represents a monovalent anion or a divalent anion;

and

m: represents 1 or 2.

50. The process of Claim 49, wherein the anion is derived from a C_6-C_{12} organic acid.

51. The process of Claim 49, wherein the anion is selected from the group consisting of an acetylacetonate, an acetate, a hexanoate, an octoate, an oxalate, a tartrate, a stearate, a sorbate, an adipate and a naphthenate.

52. The process of Claim 48, wherein the substantially anhydrous cobalt salt comprises cobalt octoate.

53. The process of Claim 48, wherein the organo-aluminium halide compound comprises a compound corresponding to the general formula:

$$R_pAlX_q$$

wherein:

R: represents a C_2-C_{12} alkyl group;

X: represents a halogen;

and

the sum of p + q equals 3.

54. The process of Claim 48, wherein said organo-aluminium halide compound is selected from the group consisting of a dialkyl aluminium chloride compound, an alkyl aluminium sesquichloride compound and mixtures thereof.

55. The process of Claim 48, wherein the organo-aluminium halide compound is selected from:

(I) a mixture of:

(a) an alkyl aluminium chloride selected from the group consisting of diethyl aluminium chloride and ethyl aluminium sesquichloride,

and

(b) an organo aluminium compound corresponding to the formula:

R_3Al

wherein:

R: represents a C_8-C_{12} alkyl group;

and

(II) an alkyl aluminium chloride wherein the alkyl group has from 8 to 12 carbon atoms.

56. The process of Claim 48, wherein the organo aluminium halide comprises a mixture of:

(a) an alkyl aluminium chloride selected from the group consisting of diethyl aluminium chloride and ethyl aluminium sesquichloride,

and

(b) an organo aluminium compound corresponding to the formula:

R_3Al

wherein:

R: represents a C_8-C_{12} alkyl group.

57. The process of Claim 55, wherein the organo aluminium compound corresponding to the formula R_3Al is present in an amount of from 0 to 1% by weight of the mixture.

58. The process of Claim 55, wherein the organo aluminium compound corresponding to the formula R_3Al comprises tri-octyl aluminium.

59. The process of Claim 48, wherein the substantially anhydrous cobalt salt comprises cobalt octoate and the organo-aluminium halide compound comprises a mixture of diethyl aluminium chloride and tri-octyl aluminium.

60. The process of Claim 59, wherein the molar ratio of cobalt octoate to the total of diethyl aluminium chloride plus tri-octyl aluminium is from about 1:15 to about 1:30.

61. The process of Claim 59, wherein the molar ratio of chlorine in diethyl aluminium chloride to the total aluminium in diethyl aluminium plus tri-octyl aluminium is from about 0.7:1 to about 0.95:1.

62. The process of Claim 33, wherein the water is mixed with the polymerization diluent by a mechanical method.

63. The process of Claim 33, wherein the water is mixed with the polymerization diluent by sonic treatment.

64. The process of Claim 33, wherein the polymerization temperature is in the range of from about 5°C to about 40°C. --

REMARKS

Applicants respectfully submit that this amendment serves only to correct minor grammatical errors and remove multiple dependencies from the original claims by substituting new claims 33-64 for original claims 1-32. New Claims 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63 and 64 are supported by original Claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31 and 32, respectively. This amendment serves only to place the application in better form. No new matter has been added by this amendment.

Attached hereto is a marked-up version of the changes made to the specification and claims by the present amendment. The attached page is captioned "Version with Markings to Show Changes Made".

In view of the preceding amendments and remarks, Applicants respectfully request an early action on the merits.

Respectfully submitted,

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VERSION WITH MARKINGS TO SHOW CHANGES MADE

In the Claims:

Claims 1-32 have been cancelled.

Claims 33-64 have been added.

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GEL REDUCTION IN HIGH CIS-1,4 POLYBUTADIENE PRODUCTION PROCESS

TECHNICAL FIELD

The present invention relates to an improved process for the production of polybutadiene having a high cis-1,4 content and a reduced gel content.

BACKGROUND ART

Processes for the production of polybutadiene having a high cis-1,4 content, generally known cis-1,4-polybutadiene, are well known. Such processes include the polymerization of 1,3-butadiene in an inert polymerization diluent using as catalyst a mixture of a transition metal salt, such as a cobalt salt, an aluminum alkyl halide or a mixture aluminum alkyl halides and water. During such processes, same gel is produced, such gel being essentially insoluble particles containing cross-linked polybutadiene. The gel is not a desirable component due to the problems it can cause to equipment used for the production of the polymer and due to the problems it can cause relating to the quality of the cis-1,4-polybutadiene.

It is thus desirable to minimize and reduce to the lowest level possible the extent of gel formation during the polymerization process.

United States patent 3,094,514 teaches a process for the production of a cis-1,4-polybutadiene, having a cis-1,4-content greater than 90 per cent. Generally, the process comprises polymerization of 1,3-butadiene in a hydrocarbon diluent in the presence as catalyst of an anhydrous dihalide diluent cobalt salt, a monoalkyl aluminum, and dialkyl aluminum monohalide. A similar type of process is described in United States patent 3,135,725. United States patent 3,646,001 teaches that cis-1-4-polybutadiene may be produced by polymerizing 1,3-butadiene in the presence of cobalt octoate and diethyl aluminum chloride which have been reacted with benzene containing water. United States patent 4,224,426 teaches the polymerization of 1,3-butadiene to produce cis-1,4-polybutadiene

in the presence of a cobalt compound, at least one organo-aluminum chloride and water, the polymerization diluent being a mixture of C_5-C_8 cycloalkane, a saturated aliphatic hydrocarbon or an α-monoolefin, and an alkyl substituted benzene having 1 to 4 alkyl substituents. United States patent 5,397,851 teaches a process for the production of a cis-1,4-polybutadiene by the polymerization of 1,3-butadiene in an inert hydrocarbon diluent in the presence as catalyst of a diluent cobalt salt, an alkyl aluminum chloride, a tri-alkyl aluminum compound and water.

DISCLOSURE OF THE INVENTION

An objective of this invention is a process for the production of a high cis-1,4-polybutadiene having a very low level of gel content.

Accordingly, in one of its aspects, the present invention provides a process for the production of cis-1,4-polybutadiene having a low level of gel content, the process comprising the step of polymerizing 1,3 butadiene in the presence of a catalyst and a polymerization diluent, the polymerization diluent comprising an organic solvent and water particles having a median particle size less than or equal to about 10 μm.

In one of its preferred embodiments, the present invention provides a process for the preparation of an essentially linear cis-1,4-polybutadiene having a very low level of gel content, the process comprising polymerizing 1,3-butadiene in the presence of a cobalt salt-organo aluminum halide-water catalyst system, the improvement being that the polymerization is carried out in the presence as polymerization diluent of a mixture of a C_5-C_6 cycloalkane and butene-1, a cobalt salt of an organic acid having 6 to 12 carbon atoms in the organic acid, an organo aluminum halide selected from (I) a mixture of (a) an alkyl aluminum chloride selected from diethyl aluminum chloride and ethyl aluminum sesqui chloride and (b) an organo aluminum or formula R_3 Al wherein R is an alkyl group having 8 to 12 carbon atoms and (II) an alkyl aluminum chloride wherein the alkyl group has 8 to 12 carbon atoms, a polymerization modifier selected from 1,2-butadiene and 1,3-cyclo

octadiene, and water, said water having been mixed with at least a portion of said polymerization diluent such that the water is present in said polymerization diluent as particles having a median particle size less than or equal to about 10 μm.

Thus, the present inventor has discovered that controlling the median particle size of the water used in the diluent surprisingly and unexpectedly results in the production of high cis-1,4-polybutadiene having a relatively low level of gel content. Thus, the median diameter of the water particles used in the polymerization diluent is less than or equal to about 10 μm. Preferably, the water is present in said polymerization diluent as particles having a median particle size in the range of from about 0.5 μm to about 8 μm, more preferably from about 0.5 μm to about 6 μm, most preferably from about 1 μm to about 5 μm. The median particle size of the water particles may be determined in a conventional manner, for example, using a Mastersizer™ particle size measuring system commercially available from Malvern Instruments Inc.

BEST MODE FOR CARRYING OUT THE INVENTION

Thus, the present process relates to the use of a polymerization diluent comprising an organic solvent and water particles.

Preferably, the organic solvent is selected from the group comprising an aliphatic compound, an aromatic compound and mixtures thereof. The aliphatic compound may be selected from a saturated hydrocarbon, an unsaturated hydrocarbon and mixtures thereof.

Preferred saturated hydrocarbons may be selected from the group comprising C_4-C_{10} aliphatic hydrocarbon, a C_5-C_{10} cyclic aliphatic hydrocarbon, a C_6-C_9 aromatic hydrocarbon, a C_2-C_{10} monoolefinic hydrocarbon and mixtures thereof.

Non-limiting examples of a suitable C_4-C_{10} aliphatic hydrocarbon may be selected from the group comprising butane, pentane, hexane, heptane, octane and mixtures thereof.

Non-limiting examples of a suitable C_2-C_{10} monoolefinic hydrocarbon may selected from the group comprising butene-1, pentene-1, hexene-1 and mixtures thereof.

Non-limiting examples of a suitable C_5-C_{10} cyclic aliphatic hydrocarbon may be selected from the group comprising unsubstituted cycloalkanes, methyl substituted cycloalkanes, ethyl substituted cycloalkanes and mixtures thereof.

Non-limiting examples of a suitable C_5-C_{10} cyclic aliphatic hydrocarbon is selected from the group comprising cylcopentane, cyclohexane, cyclooctane and mixtures thereof.

Non-limiting examples of a suitable a C_6-C_9 aromatic hydrocarbon may be selected from the group comprising benzene, toluene, xylene and mixtures thereof.

The most preferred organic solvent for use in the present process comprises a mixtures of cyclohexane and butene-1.

Preferably, the polymerization diluent further comprises a polymerization modifier. The use of such a modifier allows for controlling the molecular weight of the polymer product. Illustrative examples of useful polymerization modifiers for use in the present process may selected from the group comprising C_2-C_{18} non-conjugated dienes, C_6-C_{12} cyclic dienes and mixtures thereof. Non-limiting examples of suitable polymerization modifiers may be selected from the group comprising 1,2-butadiene, 1,3-cyclooctadiene, 1,5-cyclooctadiene and mixtures thereof. The amount of polymerization modifier may be from about 1.6 to about 3.5, preferably from about 1.95 to about 3.0, millimols per mole of 1,3-butadiene in the polymerization mixture.

The choice catalyst that is employed in butadiene polymerization art are well known. Preferably, the catalyst comprises a substantially anhydrous cobalt salt and an organo-aluminum halide compound.

The substantially anhydrous cobalt salt may comprise a compound having the formula CoA_m, wherein A is selected from a monovalent anion and a divalent anion, and m is 1 or 2. Preferably, the anion is derived from a C_6-C_{12} organic acid. Thus, non-limiting examples of usefully such anions may be selected from the group comprising an acetylacetonate, an acetate, a hexanoate, an octoate, an oxalate, a tartrate, a stearate, a sorbate, an adipate and a naphthenate.

The most preferred substantially anhydrous cobalt salt for use in the present process is cobalt octoate.

Preferably, the organo-aluminum halide compound comprises a compound having the formula:

$$R_pAlX_q$$

wherein: R is a C_2-C_{12} alkyl group, X is a halogen and p+q is 3.

More preferably, the organo-aluminum halide compound is selected from the group comprising a dialkyl aluminum chloride compound, an alkyl aluminum sesquichoride compound and mixtures thereof.

Even more preferably, the organo-aluminum halide compound is selected from:

(I) a mixture of: (a) an alkyl aluminum chloride selected from diethyl aluminum chloride and ethyl aluminum sesquichloride (this may be achieve by a mixture containing approximately equimolar amounts of diethyl aluminum chloride and ethyl aluminum dichloride), and (b) an organo aluminum compound of formula R_3Al wherein R is C_8-C_{12} alkyl group (e.g., trioctyl aluminum, tridecyl aluminum and the like); and

(II) an alkyl aluminum chloride wherein the alkyl group has 8 to 12 carbon atoms (e.g., dioctyl aluminum chloride, didecyl aluminum chloride and the like).

Embodiment (I) is more preferred. In this preferred embodiment, it is especially preferred to use the organo aluminum compound of formula R_3Al is present in an amount of 0 to 1 percent by weight of the mixture of (I) and (II). The preferred organo aluminum compound of formula R_3Al comprises tri-octyl aluminum.

The preferred catalyst system for use in the present process comprises a cobalt salt selected from cobalt octoate and cobalt naphthenate, and an organo aluminum halide compound selected from: (i) a mixture of diethyl aluminum chloride and one or more of trioctyl aluminum, tridecyl aluminum and tridodecyl aluminum, and (ii) one or more of dioctyl aluminum chloride, didecyl aluminum chloride and didodecyl aluminum chloride.

In a preferred process, using cyclohexane and butene-1 as the diluent the weight ratio of butene-1 in the cyclohexane-butene-1 mixture may be from about 24 to about 40, preferably from about 24 to about 38 and most preferably from about 34 to about 36, weight percent. A preferred catalyst cobalt octoate which is used with a preferred organo aluminum halide compound which is a mixture of diethyl aluminum chloride and trioctyl aluminum, wherein the molar ratio of cobalt octoate to the total of the diethyl aluminum chloride plus trioctyl aluminum is from about 1:15 to about 1:30, preferably from about 1:15 to about 1:20 and wherein the molar ratio of chlorine in the diethyl aluminum chloride to the total aluminum in the diethyl aluminum chloride plus trioctyl aluminum is from about 0.7:1 to about 0.95:1, preferably from about 0.8:1 to about 0.9:1.

The amount of 1,3-butadiene in the 1.3-butadiene plus diluent mixture may be from about 15 to about 35, preferably from about 25 to about 35, weight percent.

The polymerization mixture also contains water. The amount of water is from about 0.3 to about 0.8, preferably from about 0.5 to about 0.65, millimols per millimol of the alkyl aluminum chloride used. The water is mixed with at least a portion of the polymerization diluent. Accordingly, in the preferred diluent comprising cycloalkane and butene-1, the water may be mixed with cycloalkane alone, or, preferably with cycloalkane and butene-1 mixture. The mixing of the water with the polymerization diluent is such that the water as present in the polymerization diluent as particles having a median particle size equal to or less than 10 μm. Because of the very low solubility of water in hydrocarbons, including the polymerization diluents, and because of the long time to achieve a solution of water in such hydrocarbons, it is desirable for the present polymerization system to disperse the water in the polymerization diluent as very small particles to provide as high as possible a surface area to weight ratio for the particles so that interaction with the aluminum compound(s) is as efficiently as possible - this is believed to be important in reducing the amount of gel in the polybutadiene produced. The dispersion of water in the polymerization diluent may be achieved by various means such as, but not limited to, mechanical methods and sonic treatment. The improvement of the present invention is not dependent on the method used to obtain the dispersion of water in the polymerization diluent and is only dependent on the median diameter of the water particles used in the polymerization diluent being less than or equal to about 10 μm. Preferably, the water is present in said polymerization diluent as particles having a median particle size in the range of from about 0.5 μm to about 8 μm, more preferably from about 0.5 μm to about 6 μm, most preferably from about 1 μm to about 5 μm.

The polymerization may be undertaken at a temperature of from about -10°C to abut 50°C, preferably from about 5°C to about 40°C and most preferably from about 15°C to about 35°C. The polymerization process may be carried out in a batch process or in a continuous process, the continuous process being preferred. The reaction time for the

polymerization may be from about 20 to about 90 minutes, preferably from about 25 to about 60 minutes. However, the reaction time is not a critical aspect of the process and may be affected by the desired conversion of the 1,3-butadiene to polymer which may range from about 40 to about 90 percent.

The gel content of the polymer may be determined by a method in which the gel is separated from a solution of the polymer in styrene and weighed. In detail, approximately 50 g of polymer, accurately weighed, is dissolved in pure, filtered styrene to produce an approximately 4 weight percent by volume solution. The polymer-styrene mixture is shaken for 4 to 5 hours, then allowed to stand for 10 minutes and then filtered through a previously weighed filtration screen of 400 mesh. The filtration screen is then weighed again and the amount of wet gel is calculated as parts per million by weight based on the original weight of polymer used. Gel contents of less than about 250 ppm are desirable and less than about 150 ppm are more desirable and less than about 100 ppm are most desirable. In order to provide the greatest accuracy to the gel content of the polymer, normally at least three and up to 5 samples of the polymer are used to provide the corresponding number of gel content measurements.

In the following examples, the 1,3-butadiene was obtained from Union Carbide, the cyclohexane and butene-1 was Phillips pure grade and all three were passed through a column containing 4A molecular sieves followed by passage through a column containing 13X molecular sieves before use in polymerization. The 1,3-cyclooctadiene was used as a 20 weight percent solution in cyclohexane from Aldrich Chemical Company. Diethyl aluminum chloride in hexane as a 1 molar solution was from Albemarle Corporation and Akzo Nobel. Tri-octyl aluminum in heptane (20% wt.) was obtained from Albemarle Corporation as a 25.3 wt.% solution. Cobalt octoate was obtained from Mooney Chemical Inc. and used as a 6% cobalt solution in cyclohexane. Diethyl aluminum chloride was mixed with tri-octyl aluminum in sealed bottles under an inert gas in such ratios as to

provide a solution having an average composition of $Et_{1.8}Oct_{0.3}Al_1Cl_{0.9}$ in cyclohexane which was used in all examples and is referred to as M-DEAC. Polymerization was undertaken in sealed 1 litre polymerization bottles at a temperature of 27°C for 40 minutes at the end of which time the polymerization was stopped by the injection of 5 ml of ethanol containing required amount of stabilizer and the polymer was recovered by steam coagulation.

Embodiments of the present invention will be illustrated with reference to the following Examples which should not be used to limit or construe the scope of the invention.

EXAMPLE 1

Using 1 liter glass bottles capped with gasketted crown caps, 110 g of cyclohexane, 80 g of 1,3-butadiene, 60 g of butene-1, 1.8 mL of a 20% solution of 1,3-octadiene in cyclohexane, 0.01 mL of pure distilled water, 0.54 mL of a 25% solution of M-DEAC and 0.19 mL of a 0.25% solution of cobalt octoate in cyclohexane were charged to the glass bottles. When the cobalt octoate was added, the glass bottles were placed in an agitated polymerization bath maintained at 27°C for 40 minutes, followed by addition of ethanol to stop polymerization. The polymer was recovered and dried and samples used to measure the gel content, with the results shown in Table 1.

With reference to Table 1, Experiment #1 is a control in which the cyclohexane plus water was shaken for 5 minutes which produced clearly visible particles (median much greater than 10 μm) of water in the cyclohexane. The other components were added after the shaking.

In Experiment #2, the cyclohexane and water was subjected to sonification for 5 minutes in a Branson™ ultrasonic cleaner which produced a mixture of water particles in cyclohexane in which the water particles had a median particle size of less than 10 μm. The other components were added after completion of the ultrasonic mixing.

In Experiment #3, the cyclohexane, 1,3-butadiene, butene-1 and water were subjected to sonification as described above; the water particles had a median particle size of less than 10 μm. The other components were added on completion of the ultrasonic mixing.

In Experiment #4, the cyclohexane, 1,3-butadiene, butene-1 and water were subjected to shaking for 48 hours producing water particles having a median particle size of less than 10 μm. The other components were added on completion of the shaking. The gel data provided in Table 1 clearly show that the presence of water particles having a median particle size of less than 10 μm resulted in the production of polymers having significantly reduced gel contents.

TABLE 1

Experiment #	1	2	3	4
Gel (ppm)	1200	15	80	95
	1540	28	56	82
	1010	32	110	100
	1610	26	75	73
	-	30	100	-
Average Gel (ppm)	1340	26	84	87

EXAMPLE 2

Using the procedure and components described in Example 1, polymerizations were undertaken in which the cyclohexane, 1,3-butadiene, butene-1, water and M-DEAC were mixed by shaking for a period ranging from 0 to 30 minutes. The other components were added on completion of the shaking. The gel results shown in Table 2 show that when the median

particle size is reduced less than 10 μm, the gel content of the polymer is significantly reduced.

TABLE 2

Shaking Time (min)	Water Particle Size (μm)	Gel (ppm)
0	-	2950
5	-	1680
10	-	863
15	-	520
20	-	120
25	< 10	50
30	< 10	38

EXAMPLE 3

Using the procedure described in Example 1, the following experiments were undertaken. 110 g of cyclohexane and 0.011 mL of water was subjected to sonification for 5 minutes producing a mixture containing particles of water having a median particle size of less than 10 μm. Following this, 80 g of 1,3-butadiene, 2.0 mL of a 20% solution of 1:3 cyclooctadiene in cyclohexane, 60 g of butene-1, 1.25 mL of a 12% solution of diethyl aluminum chloride in cyclohexane and 0.2 mL of a 0.25% solution of cobalt octoate in cyclohexane were added and the contents immersed in an agitated water bath at 27°C for 40 minutes. After stopping the polymerization, the polymer was recovered and the gel content was determined to be 120 ppm. In a control experiment, the same procedure was followed except that instead of being sonified, the cyclohexane and water

was mixed by shaking. The water particles were found to have a median particle size of greater than 10 μm. The resulting polymer was found to have a gel content of greater than 3000 ppm.

All publications, patents and patent applications referred to herein are incorporated by reference in their entirety to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated by reference in its entirety.

What is claimed is:

1. A process for the production of cis-1,4-polybutadiene having a low level of gel content, the process comprising the step of polymerizing 1,3 butadiene in the presence of a catalyst and a polymerization diluent, the polymerization diluent comprising an organic solvent and water particles having a median particle size less than or equal to about 10 μm.

2. The process defined in claim 1, wherein the water is present in said polymerization diluent as particles having a median particle size in the range of from about 0.5 μm to about 8 μm.

3. The process defined in claim 1, wherein the water is present in said polymerization diluent as particles having a median particle size in the range of from about 0.5 μm to about 6 μm.

4. The process defined in claim 1, wherein the water is present in said polymerization diluent as particles having a median particle size in the range of from about 1 μm to about 5 μm.

5. The process defined in any one of claims 1-4, wherein the organic solvent is selected from the group comprising an aliphatic compound, an aromatic compound and mixtures thereof.

6. The process defined in claim 5, wherein the aliphatic compound is selected from a saturated hydrocarbon, an unsaturated hydrocarbon and mixtures thereof.

7. The process defined in claim 6, wherein the saturated hydrocarbon is selected from the group comprising C_4-C_{10} aliphatic hydrocarbon, a C_5-C_{10}

cyclic aliphatic hydrocarbon, a C_6-C_9 aromatic hydrocarbon, a C_2-C_{10} monoolefinic hydrocarbon and mixtures thereof.

8. The process defined in claim 7, wherein the C_4-C_{10} aliphatic hydrocarbon is selected from the group comprising butane, pentane, hexane, heptane, octane and mixtures thereof.

9. The process defined in claim 7, wherein the C_2-C_{10} monoolefinic hydrocarbon is selected from the group comprising butene-1, pentene-1, hexene-1 and mixtures thereof.

10. The process defined in claim 7, wherein the C_5-C_{10} cyclic aliphatic hydrocarbon is selected from the group comprising unsubstituted cycloalkanes, methyl substituted cycloalkanes, ethyl substituted cycloalkanes and mixtures thereof.

11. The process defined in claim 7, wherein the C_5-C_{10} cyclic aliphatic hydrocarbon is selected from the group comprising cylcopentane, cyclohexane, cyclooctane and mixtures thereof.

12. The process defined in claim 7, wherein the a C_6-C_9 aromatic hydrocarbon is selected from the group comprising benzene, toluene, xylene and mixtures thereof.

13. The process defined in any one of claims 1-4, wherein the organic solvent comprises a mixtures of cyclohexane and butene-1.

14. The process defined in any one of claims 1-13, wherein polymerization diluent further comprises a polymerization modifier selected from the group comprising C_2-C_{18} non-conjugated dienes, C_6-C_{12} cyclic dienes and mixtures thereof.

15. The process defined in claim 14, wherein the polymerization modifier is selected from the group comprising 1,2-butadiene, 1,3-cyclooctadiene, 1,5-cyclooctadiene and mixtures thereof.

16. The process defined in any one of claims 1-15, wherein the catalyst comprises a substantially anhydrous cobalt salt and an organo-aluminum halide compound.

17. The process defined in claim 16, wherein the substantially anhydrous cobalt salt comprises a compound having the formula CoA_m, wherein A is selected from a monovalent anion and a divalent anion, and m is 1 or 2.

18. The process defined in claim 17, wherein the anion is derived from a C_6-C_{12} organic acid.

19. The process defined in claim 17, wherein the anion is selected from the group comprising an acetylacetonate, an acetate, a hexanoate, an octoate, an oxalate, a tartrate, a stearate, a sorbate, an adipate and a naphthenate.

20. The process defined in claim 16, wherein the substantially anhydrous cobalt salt comprises cobalt octoate.

21. The process defined in any one of claims 16-20, wherein the organo-aluminum halide compound comprises a compound having the formula:

$$R_pAlX_q$$

wherein: R is a C_2-C_{12} alkyl group, X is a halogen and p+q is 3.

22. The process defined in any one of claims 16-20, wherein organo-aluminum halide compound is selected from the group comprising a dialkyl

aluminum chloride compound, an alkyl aluminum sesquichoride compound and mixtures thereof.

23. The process defined in any one of claims 16-20, wherein the organo-aluminum halide compound is selected from:

(I) a mixture of: (a) an alkyl aluminum chloride selected from diethyl aluminum chloride and ethyl aluminum sesquichloride and (b) an organo aluminum compound of formula R_3Al wherein R is C_8-C_{12} alkyl group; and

(II) an alkyl aluminum chloride wherein the alkyl group has 8 to 12 carbon atoms.

24. The process defined in any one of claims 16-20, wherein the organo aluminum halide comprises a mixture of: (a) an alkyl aluminum chloride selected from diethyl aluminum chloride and ethyl aluminum sesquichloride and (b) an organo aluminum compound of formula R_3Al wherein R is C_8-C_{12} alkyl group.

25. The process defined in any one of claims 23-24, wherein the organo aluminum compound of formula R_3Al is present in an amount of 0 to 1 percent by weight of the mixture.

26. The process defined in any one of claims 23-24, wherein the organo aluminum compound of formula R_3Al comprises tri-octyl aluminum.

27. The process defined in claim 16, wherein the substantially anhydrous cobalt salt comprises cobalt octoate and the organo-aluminum halide compound comprises a mixture of diethyl aluminum chloride and tri-octyl aluminum

28. The process defined in claim 27, wherein the molar ratio of cobalt octoate to the total of diethyl aluminum chloride plus tri-octyl aluminum is from about 1:15 to about 1:30.

29. The process defined in claim 27, wherein the molar ratio of chlorine in diethyl aluminum chloride to the total aluminum in diethyl aluminum chloride plus tri-octyl aluminum is from about 0.7:1 to about 0.95:1.

30. The process defined in any one of claims 1-29, wherein the water is mixed with the polymerization diluent by a mechanical method.

31. The process defined in any one of claims 1-29, wherein the water is mixed with the polymerization diluent by sonic treatment.

32. The process defined in any one of claims 1-31, wherein the polymerization temperature is in the range of from about 5° to about 40°C.

Attorney Docket No. ______

COMBINED DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

My residence, post office and address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

"GEL REDUCTION IN HIGH CIS-1,4 POLYBUTADIENE PRODUCTION PROCESS"

the specification of which (check one)

☒ is attached hereto

☐ was filed on ______ as Application Serial No. ______ and was amended on ______ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of the application in accordance with title 37, Code of Federal Regulations, §1.56 (a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below and foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

PRIOR FOREIGN APPLICATION(S)

(Number)	(Country)	(Day/month/year filed)	Priority claimed
2,246,608	Canada	4 September 1998	☒ Yes ☐ No
			☐ Yes ☐ No
			☐ Yes ☐ No

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(STATUS: patented/pending/abandoned)

I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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